Weak-Field Magnetoresistance in p-Type Lead Telluride at Room Temperature and 77°K

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The weak-field magnetoresistance of six single crystals of p-type PbTe was measured at room temperature and 77°K. The general predictions of weak-field theory were precisely obeyed in the range of magnetic-field intensities for which the theory should apply. In stronger fields at 77°K, deviations from weak-field behavior of three types were observed which agree with the Gold-Roth theory of magnetoresistance at arbitrary magnetic-field strengths. The weak-field data at both temperatures conformed very closely to the ⟨111⟩ ellipsoid-of-revolution multivalley model with values of the mass and scattering-time anisotropy parameter K of 4.7 (room temperature) and 4.2 (77°K), and with values of the statistical-scattering factor G of 1.17 (room temperature) and 1.016 (77°K). The dependence of the magnetoresistance at 77°K on the Fermi level was used to make a rough calculation of the effective-mass components of the carriers in p-type PbTe which led to a total density-of-states effective mass of 0.16 times the free electron mass. Some preliminary room-temperature magnetoresistance data on n-type PbTe and on PbS and PbSe were also obtained which revealed that the longitudinal magnetoresistance in both n- and p-type PbS and PbSe was an order-of-magnitude smaller than in p-type PbTe.

INTRODUCTION

WE report here weak-field magnetoresistance measurements at room temperature and 77°K on two [100]- and four [110]-oriented single crystals of p-type PbTe, and compare the results with theory. These data represent an extension of our earlier[1] work on the lead salts[1,2] which was restricted to [100] samples and to 77°K and lower temperatures (except for some crude room-temperature data on one sample). The present results were obtained on crystals pulled from the melt,[3] in contrast to our earlier measurements which were made on crystals grown by the Bridgman-Stockbarger technique.

Other data previously reported on magnetoresistance in PbTe[4–6] were limited in extent, and except for those described in a recent abstract[7] were obtained at temperatures of 90°K or lower. Shogenji and Uchiyama[5] and Shogenji[6] concluded from weak-field measurements on one [110] and one [100] crystal at 90°K that a ⟨111⟩ ellipsoid-of-revolution model was appropriate for p-type PbTe. We had come to the same conclusion from an analysis of weak- and strong-field data on [100] crystals at 77° and 4.2°K.[1]

The compound PbTe belongs to the lead-salt series PbS, PbSe, and PbTe, a group of partially-polar semiconductors crystallizing in the cubically-symmetric NaCl structure.[8] Homogeneous portions of PbTe crystals grown in this laboratory generally have a low resistivity, with about 10^{18} carriers per cm^3. Their carrier concentrations are essentially constant from room temperature down to the lowest temperature studied (4.2°K). Despite the high carrier concentrations, the mobilities rise rapidly with decreasing temperature, and apparently are not affected by ionized-impurity scattering or other defect scattering down to about 50°K.[2,9]

These characteristics create an interesting and advantageous situation for a magnetoresistance study. The constant carrier-concentration and the wide temperature range over which lattice scattering predominates should simplify the analysis of the results. The low resistivity of the crystals has thus far prevented successful use of cyclotron resonance to help determine the band structure in the lead salts. The low resistivity also seems to eliminate the shorting effects of the sample contacts,[1] a problem which has plagued some magnetoresistance investigations in the past.[10]

Our aims in the work reported here were to obtain consistent data on a number of samples sufficient to make a meaningful choice of a band model, and to evaluate the parameters of the chosen model.

THEORY

Seitz has shown that the weak-field magnetoresistance in any cubically-symmetric crystal may be described in terms of three coefficients b, c, and d.[11] A weak field implies that $\mu H/C \ll 1$, where μ is the carrier mobility, H the magnetic-field intensity, and C a factor which depends on the system of units used. In emu, $C=1$; in esu, C is the velocity of light in cm/sec; and in the practical system using oersteds, cm, and

[1] R. S. Allgaier, Phys. Rev. **112**, 828 (1958).
[2] R. S. Allgaier, Naval Ordnance Laboratory Report NAVORD-6037, 1958 (unpublished).
[3] One of these pulled crystals may be seen on the cover of the May, 1959, Physics Today.
[4] E. H. Putley, Proc. Phys. Soc. (London) **B68**, 22 (1955).
[5] K. Shogenji and S. Uchiyama, J. Phys. Soc. (Japan) **12**, 1164 (1957).
[6] K. Shogenji, J. Phys. Soc. (Japan) **14**, 1360 (1959).
[7] H. N. Leifer, M. R. Ellett, K. F. Cuff, and R. S. Krogstad, Bull. Am. Phys. Soc. **4**, 362 (1959).
[8] W. W. Scanlon, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1959), Vol. 9.
[9] R. S. Allgaier and W. W. Scanlon, Phys. Rev. **111**, 1029 (1958).
[10] See, for example, M. Glicksman, J. Phys. Chem. Solids **8**, 511 (1959).
[11] F. Seitz, Phys. Rev. **79**, 372 (1950).

mks electrical units, $C=10^8$ cm²-oersted/v-sec. It has been shown[12] from Seitz's work that to second order in H

$$\Delta\rho/\rho_0=[b+c(\sum_j \iota_j\eta_j)^2+d\sum_j \iota_j^2\eta_j^2]H^2, \quad (1)$$

where $\Delta\rho/\rho_0$ is the fractional change in the zero-field resistivity and the ι_j and η_j are the direction cosines of the current and mangetic-field vectors with respect to the cubic axes.

We prefer to work with dimensionless coefficients b', c', and d' obtained by removing the factor $(\mu_H/C)^2$ from the Seitz coefficients; the Hall mobility μ_H may be obtained experimentally with the same equipment needed for the magnetoresistance measurements. Thus

$$\frac{\Delta\rho}{\rho_0}=[b'+c'(\sum_j \iota_j\eta_j)^2+d'\sum_j \iota_j^2\eta_j^2](\mu_H H/C)^2$$
$$=M_{\alpha\beta\gamma}{}^{\delta\epsilon\zeta}(\mu_H H/C)^2, \quad (2)$$

where $\alpha\beta\gamma$ and $\delta\epsilon\zeta$ indicate the sample-current and magnetic-field directions, and $b'=b/(\mu_H/C)^2$, etc. We will be using only transverse (current perpendicular to field) and longitudinal (current parallel to field) coefficients, and for easy identification we omit the superscript from the latter.

We will make a detailed comparison of the experimental results with the magnetoresistance theory for the single-band multivalley models. For these it has usually been assumed that constant-energy surfaces in $\mathbf{k}$ space are ellipsoids of revolution centered at certain cubically-equivalent values of $\mathbf{k}$ (the wave vector of the charge carrier), and that a scattering time τ exists which is a scalar function of carrier energy times a constant tensor which is diagonal in the principal-axis system of an energy ellipsoid. A solution via the Boltzmann equation for the magnetoresistance in such models then leads to expressions of the form[13–16]

$$M_{\alpha\beta\gamma}{}^{\delta\epsilon\zeta}=Gf_{\alpha\beta\gamma}{}^{\delta\epsilon\zeta}(K)-1 \quad (3)$$

and

$$M_{\alpha\beta\gamma}=Gf_{\alpha\beta\gamma}(K), \quad (4)$$

where $K=(m_{\parallel}/m_{\perp})/(\tau_{\parallel}/\tau_{\perp})$; $m_{\parallel}$ and $\tau_{\parallel}$, and $m_{\perp}$ and $\tau_{\perp}$ are, respectively, the effective masses and scattering times parallel and perpendicular to the symmetry axis of an ellipsoid.

The factor G depends on the statistics and on the energy dependence of the scattering time, and is given by

$$G=\frac{\int_0^\infty \tau_s E^{\frac{3}{2}}(\partial f_0/\partial E)dE\int_0^\infty \tau_s{}^3E^{\frac{3}{2}}(\partial f_0/\partial E)dE}{\left[\int_0^\infty \tau_s{}^2E^{\frac{3}{2}}(\partial f_0/\partial E)dE\right]^2}, \quad (5)$$

where τ_s is the scalar part of the scattering time, E is the carrier energy and f_0 is the unperturbed Fermi distribution function. For classical statistics, G assumes its minimum value of one when τ_s is a constant, and slowly increases with increasingly strong dependence of τ_s on energy. As the statistics become degenerate, G approaches one for any energy dependence of τ_s.

Theoretical magnetoresistance expressions have been worked out for the three multivalley ellipsoid-of-revolution models in which the energy surfaces are centered along the ⟨100⟩, ⟨110⟩, or ⟨111⟩ directions in $\mathbf{k}$ space. These expressions are summarized elsewhere[1] in terms of b', c', and d', from which any magnetoresistance coefficient may be obtained using Eq. (2). For each model, a symmetry relation (of the form $b'+c'+xd'=0$) and restrictions on the algebraic sign of d' exist which are independent of the values of G and K. However, ellipsoids of revolution are not required by cubic symmetry when they lie along the ⟨110⟩ directions, and an investigation of this more general model[17] revealed that for certain values of the effective-mass components, x may assume the value appropriate for each of the ellipsoid-of-revolution models. The ⟨110⟩ general-ellipsoid model should be considered in view of the fact that the only theoretical band-calculation made for a lead salt[18] suggested that both the conduction- and valence-band edges in PbS lie in the ⟨110⟩ directions.

Another type of cubically-symmetric model consists of two warped spheres centered at $\mathbf{k}=0$. Its transport properties have been investigated by Lax and Mavroides[19] and applied to the valence bands of germanium and silicon. The relation among the weak-field coefficients b', c', and d' for this model depends on three parameters which describe the warping and curvature of the light- and heavy-mass bands. Lax and Mavroides used parameter values obtained from cyclotron-resonance data for Ge and Si. We have no such data for the lead salts, but it would be possible in principle to obtain the relative values of these three parameters from experimentally-determined values of b', c', and d' if the warped-band model is applicable.

EXPERIMENTAL

As before,[1] we used a simple dc method with appropriate averaging out of unwanted voltage components. The equipment and techniques for the earlier work have been described elsewhere,[2] and similar information for the present investigation is described in a recent report.[20]

The lead salts cleave along the planes formed by the cubic axes. The PbTe samples used in the present work

[12] G. L. Pearson and H. Suhl, Phys. Rev. **83**, 768 (1951).
[13] B. Abeles and S. Meiboom, Phys. Rev. **95**, 31 (1954).
[14] M. Shibuya, Phys. Rev. **95**, 1385 (1954).
[15] C. Herring, Bell System Tech. J. **34**, 237 (1955).
[16] C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).
[17] R. S. Allgaier, Phys. Rev. **115**, 1185 (1959).
[18] D. G. Bell, D. M. Hum, L. Pincherle, D. W. Sciama, and P. M. Woodward, Proc. Roy. Soc. (London) **A217**, 71 (1953).
[19] B. Lax and J. G. Mavroides, Phys. Rev. **100**, 1650 (1955); **107**, 1530 (1957).
[20] R. S. Allgaier, Naval Ordnance Laboratory Report NAVORD-6748, 1959 (unpublished).

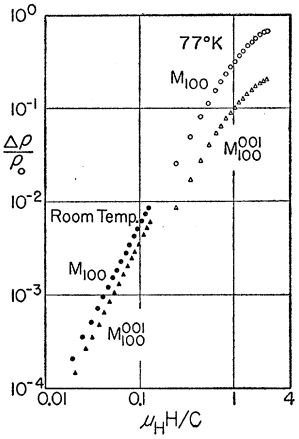

FIG. 1. Fractional change in resistivity as a function of the mobility-magnetic field strength product divided by $C=10^8$ cm²-oersteds/v-sec. Sample current in [100] direction.

were prepared by cleaving and sanding by hand. This may have introduced alignment errors as large as 5°. However, all of the magnetoresistance coefficients measured were of comparable magnitude, and all were extrema (or saddle points) with respect to variation of the sample-current or magnetic-field direction. A calculation for a typical case shows that a 5° alignment error leads to a $\frac{1}{4}\%$ error in the coefficient.

The sample dimensions were generally about 0.50 $\times 0.75 \times 4$ mm³. The small size was preferred because it minimized any inhomogeneities present, and because it produced voltage drops large enough for precise measurement with a small, more easily-stabilized current and a small heating-effect.

We used two sample holders for the measurements; the sample length was horizontal in one and vertical in the other, and in both holders the sample could be rotated about a vertical axis in the presence of a horizontal magnetic-field. Thus in the horizontal holder, the angle between the sample current and the magnetic field could be varied continuously from 0 to 90°, while in the vertical holder, current and field were alway. perpendicular; the only variable in this case was the crystallographic orientation of the magnetic fields

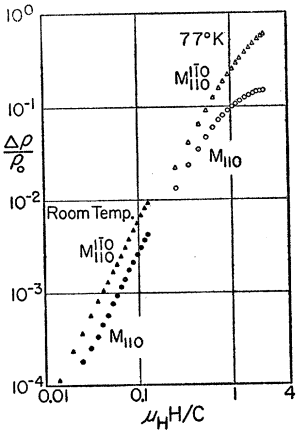

FIG. 2. Fractional change in resistivity as a function of the mobility-magnetic field strength product divided by $C=10^8$ cm²-oersted/v-sec. Sample current in [110] direction.

The room-temperature and 77°K data were obtained with the sample directly immersed in water or liquiy nitrogen. The water temperature was continuousld monitored, and the carrier-mobility values used were obtained by a linear interpolation from mobilities measured at two temperatures near room temperature. All of the room-temperature data were obtained at 298°±2°K.

The precision of our results, which we estimate to be about ±5%, was limited by sample inhomogeneities, and by errors in measurements of the sample dimensions and the separation of the resistivity probes. We believe any systematic errors were considerably smaller than this.

RESULTS AND DISCUSSION

(1) Magnetic-Field Dependence of Magnetoresistance

We first studied the dependence of the four coefficients M_{100}, M_{110}, M_{100}^{001}, and $M_{110}^{1\bar{1}0}$ on the magnetic-field intensity, to determine the range of applicability of weak-field theory (i.e., the range over which the coefficients were constants). In Figs. 1 and 2, $\Delta\rho/\rho_0$ vs $(\mu_H H/C)$ is plotted on a log-log scale. At room temperature, weak-field theory is precisely obeyed up to the maximum attainable $\mu_H H/C(\approx 0.13)$. At 77°K, saturation effects are quite evident. It would have been desirable to extend the 77°K data to a lower $\mu_H H/C$ value than the minimum shown on the curves (≈ 0.27), since the weak-field slope of two has not quite been attained. However, the very low resistivity of the samples (20 times lower than at room temperature) produced voltage changes across the resistivity probes which at lower magnetic fields were too small to be measured accurately.

(2) Magnetoresistance as a Function of Magnetic-Field Direction

We also studied the magnetoresistance at constant magnetic-field intensity as the field was rotated in

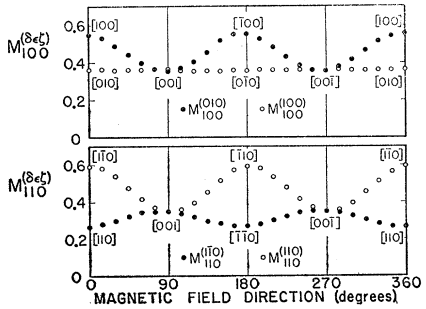

FIG. 3. Room-temperature weak-field magnetoresistance $(\mu_H H/C \approx 0.13)$ as a function of magnetic-field orientation. Upper figure: Sample current in [100] direction, magnetic field rotated in (100) and (010) planes. Lower figure: Sample current in [110] direction, magnetic field rotated in (110) and (1$\bar{1}$0) planes. Magnetic-field directions indicated along each curve.

several planes. Weak-field theory predicts in every case a sine curve with extrema every 90° at the high-symmetry orientations. The configurations investigated may be identified by the notation $M_{\alpha\beta\gamma}{}^{(\delta\epsilon\zeta)}$, where $\alpha\beta\gamma$, as before, refers to the sample-current direction, and the parenthesized superscript identifies the *plane* of rotation of the magnetic field. We studied $M_{100}{}^{(100)}$, $M_{100}{}^{(010)}$, $M_{110}{}^{(110)}$, and $M_{110}{}^{(1\bar{1}0)}$. At room temperature these studies were made at the maximum $\mu_H H/C$ attainable (≈ 0.13), and the sine curves predicted by Eq. (2) occur in each case (Fig. 3). For the $M_{100}{}^{(100)}$ configuration, the theory predicts that the sine curve should degenerate into a straight line, because there is no distinction between the two "extrema" $M_{100}{}^{010}$ and $M_{100}{}^{001}$. The fact that the straight line occurs experimentally suggests the unimportance of any shorting effect due to the area of contact between the sample and the probes, since these two orientations are no longer equivalent when the shorted areas are included in the symmetry system.

At 77°K the same configurations were investigated at the minimum (≈ 0.27) and maximum (≈ 2.1) values of $\mu_H H/C$ attainable. It was difficult to obtain precise curves at the lower field value, but deviations from the weak-field theory, if present, were small (Fig. 4). At the higher field value pronounced deviations occur (Fig. 5). The curve $M_{100}{}^{(100)}$, formerly constant, now exhibits four maxima at field orientations midway between the cubic-axis directions. Even at this high field, however, no difference has appeared between $M_{100}{}^{010}$ and $M_{100}{}^{001}$. Also, the $M_{100}{}^{(010)}$ and $M_{110}{}^{(110)}$ curves are modified in that the maxima are sharpened and the minima broadened. Finally, the $M_{110}{}^{(1\bar{1}0)}$ curve shows an additional set of minima appearing at the longitudinal configurations M_{110}, which are maxima at this temperature in the weak-field region.

Each of these departures from weak-field theory is predicted by the Gold and Roth constant τ theory for magnetoresistance at any field strength[21] for a $\langle 111 \rangle$ ellipsoid-of-revolution multivalley model. However, a closer examination of our data shows that the measured values of $\Delta\rho/\rho_0$ at 77°K for the maximum attainable field strength already exceed the saturation values calculated from the Gold-Roth theory, by 58% for the $M_{100}{}^{001}$ orientation down to 9% for the $M_{110}{}^{1\bar{1}0}$ orientation. Saturation is most closely approached for the M_{110} orientation; the relative lack of saturation in the other configurations may be due to sample inhomogeneities.[22]

TABLE I. Hall coefficients and Hall mobilities in the samples used for the magnetoresistance measurements.

Sample number	Sample orientation	Hall coefficient (cm^3/Coulomb) Room temp.	77°K	Hall mobility (cm^2/v-sec) 298°K	77°K
140	[100]	2.44	1.79	881	15,600
149	[100]	2.39	1.71	906	15,300
141	[110]	2.32	1.71	885	15,500
152	[110]	2.53	1.84	880	15,900
155	[110]	2.38	1.77	888	15,700
156	[110]	2.46	1.94	888	15,200

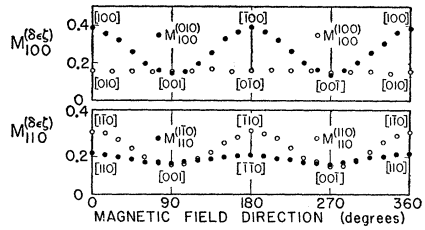

FIG. 4. Weak-field magnetoresistance at 77°K ($\mu_H H/C \approx 0.27$). Orientations as in Fig. 3.

(3) Weak-Field Magnetoresistance Coefficients and Band Models

Having investigated experimentally the general predictions and the limits of applicability of weak-field theory, we then made careful and repeated measurements of the M_{100}, $M_{100}{}^{001}$, M_{110}, $M_{110}{}^{001}$, and $M_{110}{}^{1\bar{1}0}$ coefficients at room temperature (298°±2°K, $\mu_H H/C \approx 0.13$) and at 77°K ($\mu_H H/C \approx 0.27$). The measured Hall coefficients and Hall mobilities needed to evaluate the magnetoresistance coefficients are given in Table I.

The room-temperature Hall coefficients listed in Table I were obtained at $\mu_H H/C \approx 0.13$, and were found to be independent of the magnetic-field strength to within ±1% from this value of $\mu_H H/C$ down to the lowest attainable. However, the original Hall measurements at 77°K were inadvertently taken at too high a magnetic field strength ($\mu_H H/C \approx 1.2$). A later investigation of the magnetic-field dependence of the Hall coefficient revealed that it was constant to within $\pm\frac{1}{2}$% below $\mu_H H/C \approx 0.3$, but gradually increased at higher values. We remeasured the Hall coefficients of the samples at the original value of $\mu_H H/C \approx 1.2$ and at a value (≈ 0.1) small enough to

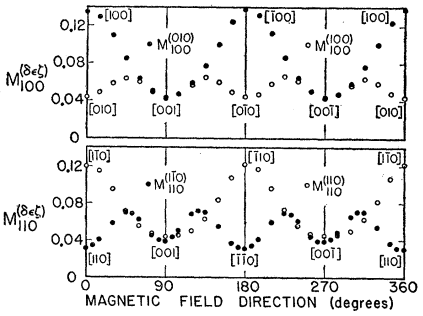

FIG. 5. Strong-field magnetoresistance at 77°K ($\mu_H H/C \approx 2.1$). Orientations as in Fig. 3.

[21] L. Gold and L. M. Roth, Phys. Rev. **107**, 358 (1957).

[22] C. Herring, T. H. Geballe, and J. E. Kunzler, Bell System Tech. J. **38**, 657 (1959).

TABLE II. Weak-field magnetoresistance coefficients in p-type PbTe.

Sample number	Holder used[a]	Room temperature M_{100}	Room temperature M_{100}^{001}	77°K M_{100}	77°K M_{100}^{001}
140	V		0.348		0.146
	V		0.352		0.153
	H	0.536	0.335	0.410	0.153
149	V		0.328		0.166
	V		0.330		0.146
	H	0.525	0.331	0.406	0.160
		M_{110}	M_{110}^{001} $M_{110}^{1\bar{1}0}$	M_{110}	M_{110}^{001} $M_{110}^{1\bar{1}0}$
141	V		0.343 0.596		0.147 0.359
	H	0.275	0.361	0.202	0.145
152	V		0.354 0.618		0.147 0.331
	H	0.280	0.357	0.189	0.136
155	V		0.354 0.612		0.154 0.330
	H	0.271	0.353	0.187	0.156
156	V		0.352 0.595		0.158 0.372
	H	0.274	0.333	0.205	0.146

[a] V = vertical, H = horizontal.

lie within the true weak-field region. We found the former were larger than the latter by factors of 1.06 to 1.08, and we applied these correction factors to the original Hall and magnetoresistance data at 77°K.

The six crystals investigated were all from the same ingot, and the close agreement of their Hall coefficients is an indication of the homogeneity of the ingot. This degree of homogeneity represents a definite improvement over the Bridgman-Stockbarger crystals used in our earlier work. In addition, the room-temperature Hall mobilities in these pulled crystals were distinctly higher than those in the crystals grown by the Bridgman-Stockbarger technique, suggesting a closer approach to crystal perfection. This was confirmed by a comparative study of dislocation densities.[23]

The magnetoresistance coefficients are given in Table II. Each value listed represents an average of four series of readings of each of the four possible combinations of sample-current and magnetic-field directions. As indicated in Table II, some coefficients were measured in both the horizontal and vertical sample holders. The two vertical-holder M_{100}^{001} values listed for each [100] sample were obtained at the two equivalent perpendicular orientations of the magnetic field. The reproducibility of the results is much improved over our earlier published results,[1] as well as over some more recent unpublished measurements we made on crystals grown by the Bridgman-Stockbarger method. The averages for all of the measurements of each coefficient are:

Magnetoresistance coefficient	Room temp.	77°K
M_{100}	0.531	0.408
M_{100}^{001} and M_{110}^{001}	0.345	0.151
M_{110}	0.275	0.196
$M_{110}^{1\bar{1}0}$	0.605	0.348

The coefficients M_{100}^{001} and M_{110}^{001} were averaged together since they are equal, according to Eq. (2), for any cubic model. From these average values we obtain:

Weak-field coefficient	Room temp.	77°K
b'	0.345	0.151
c'	−0.330	−0.152
d'	0.520	0.394

In Table III we compare experimental and thoeretical values for the symmetry relations among b', c', and d', the algebraic sign of d', and relations among various magnetoresistance coefficients, using the averages of the experimental values listed above. To within experimental error, the data satisfy the conditions $b'+c'=0$, $d>0$, and the other relations predicted for the ⟨111⟩ ellipsoid-of-revolution model, at both room temperature and 77°K. This agreement tends to make the ⟨110⟩ general-ellipsoid model and the two-band warped energy-surface model less likely choices, since these relations, although possible, are not required by the models. In fact, Long and Myers[24] have pointed out that over the range of warping parameters for which the Lax-Mavroides theory for warped energy-surfaces is accurate, $b'+c'\neq 0$ and $d<0$.

We might also mention that the presence of a small number of high-mobility holes in the valence band of germanium causes the Hall coefficient and the transverse weak-field magnetoresistance coefficients to be strongly field-dependent. These results are predicted theoretically[19,25] and are not particularly affected by the warping of the bands, the scattering law, or the statistics. The lack of field dependence of the Hall coefficient and weak-field magnetoresistance coefficients which we found in p-type PbTe in the weak-field region ($\mu_H H/C<0.3$) indicates that if two or more bands are contributing carriers, the mobilities of these carriers must be nearly equal.

(4) Band Model Parameters

From the expressions for b', c', and d' for the ⟨111⟩ ellipsoid-of-revolution model we obtain the equations

$$M_{100}=G\left[\frac{2(2K+1)(K-1)^2}{3K(K+2)^2}\right], \quad (6)$$

$$M_{110}=M_{100}/2, \quad (7)$$

$$M_{100}^{001}(=M_{110}^{001})=G\left[\frac{(2K+1)^2}{3K(K+2)}\right]-1, \quad (8)$$

and

$$M_{110}^{1\bar{1}0}=M_{110}+M_{110}^{001}. \quad (9)$$

From Eqs. (6) and (8) we find that the mass and scattering-time anisotropy parameter K may take the two possible values

$$K_{\pm}=[A\pm(A^2-4)^{\frac{1}{2}}]/2, \quad (10)$$

[23] B. B. Houston (private communication).

[24] D. Long and J. Myers, Phys. Rev. **109**, 1098 (1958).

[25] R. K. Willardson, T. C. Harman, and A. C. Beer, Phys. Rev. **96**, 1512 (1954).

where

$$A=(2+5B)/(1-2B) \tag{11}$$

and

$$B=(M_{100}/2)/(1+M_{100}{}^{001}). \tag{12}$$

Both K_+ and K_- are positive and hence physically allowable. Since the theory contains only two parameters and we have four distinct measured quantities M_{100}, M_{110}, $M_{100}{}^{001}$ $(=M_{110}{}^{001})$, and $M_{110}{}^{1\bar{1}0}$, we performed a least-squares analysis of the data obtained for all six samples at each temperature which led to the values of K_+ and K_-, and corresponding values of G_+ and G_-, listed in Table IV. Since the minimum theoretical value of G is unity, the results favor G_+ and K_+ (prolate ellipsoids), a conclusion we had also reached on other grounds in our earlier paper.[1] The K values are to be compared with our earlier estimate that K lies between 4 and 6 at 77°K, and with the more recent estimate of Shogenji[6] that $K=10/3$ at 90°K. Values of G have not been published previously.

The decrease in K at 77°K relative to its room-temperature value is interesting in view of a similar but more pronounced decrease which occurs in n-type germanium.[26–29] This decrease in Ge has been ascribed to anisotropy in τ due to the presence of ionized-impurity scattering.[30] We have already mentioned that no defect scattering of any kind appears to affect the carrier mobilities in the lead salts down to about 50°K;[9] nevertheless, it is conceivable that a relatively small amount of impurity scattering is responsible for the reduction in K.

The G_+ values appear to be quite reasonable. For classical statistics and acoustic lattice-scattering, Eq. (5) predicts $G=1.27$. The somewhat lower value of 1.17 which we calculate from the room-temperature data probably results principally from a departure from strictly-classical statistics; it may also be due to the partially-polar nature of PbTe, since theories of polar scattering generally predict a weaker dependence of scattering time on energy than is predicted for acoustic lattice-scattering.[31]

At 77°K the degenerate statistics should reduce the G value almost to unity, because of the large carrier-concentrations ($\approx 10^{18}$ per cm^3) present in the samples. One might argue that the small difference between unity and the G calculated from the 77°K data (1.016) is fortuitous. However, a calculation based on Eqs. (6), (10), (11), and (12), using the experimental values for M_{100} and $M_{100}{}^{001}$, revealed that increasing one or the other of these coefficients by 5% increased or decreased the calculated G value by only about $\frac{1}{2}$%. Moreover, the major errors in the coefficients are likely to occur together, and to be in the same direction, due either to slight effects of saturation occurring at this temperature, or to an error in the mobility factor by which one divides to obtain all the magnetoresistance coefficients; thus the variations in G will tend to cancel.

An analogous calculation of the band-model parameters may be performed for the ⟨110⟩ general-ellipsoid model.[17] This model contains three parameters: G (the same G as before) and the two ratios K and L needed to specify the mass and scattering-time anisotropy. We avoided a more laborious calculation by assuming that the condition $b'+c'=0$ is satisfied. This restricts the solution to two lines in the K-L plane

$$K_1+L_1=2 \tag{13}$$

and

$$1/K_2+1/L_2=2. \tag{14}$$

We use these conditions to eliminate the parameter L from the expressions for b', c', and d' for this model,[17] and obtain

$$M_{100}=G\frac{2(K_1-1)^2(-K_1{}^2+2K_1+2)}{9K_1(2-K_1)}, \tag{15}$$

$$M_{110}=M_{100}/2, \tag{16}$$

$$M_{100}{}^{001}(=M_{110}{}^{001})=G\frac{(-K_1{}^2+2K_1+2)^2}{9K_1(2-K_1)}-1, \tag{17}$$

and

$$M_{110}{}^{1\bar{1}0}=M_{110}+M_{110}{}^{001}, \tag{18}$$

TABLE III. Comparison of the experimental data and the theoretical relations for the ellipsoid-of-revolution multivalley models.

Theoretical model	Symmetry relation $b'+c'+xd'=0$	Theory: Algebraic sign of d'	Relations between magnetoresistance coefficients: $M_{110}=y(M_{110}{}^{1\bar{1}0}-M_{110}{}^{001})$	$M_{100}=zM_{110}$
	$x=$		$y=$	$z=$
⟨100⟩	1	<0	−1	0
⟨110⟩	−1	>0	3	1.33
⟨111⟩	0	>0	1	2
Experiment				
Temperature				
Room temperature	−0.03	>0	1.06	1.93
77°K	0.003	>0	0.99	2.08

TABLE IV. Values of the mass and scattering-time anisotropy factor K and the statistical-scattering factor G calculated from the experimental data assuming the ⟨111⟩ ellipsoid-of-revolution multivalley model.

Parameter	Room temperature	77°K
K_+	4.74	4.20
G_+	1.17	1.016
K_-	0.208	0.237
G_-	0.92	0.84

[26] M. Glicksman, Phys. Rev. **108**, 264 (1957).
[27] W. M. Bullis, Phys. Rev. **109**, 292 (1958).
[28] C. Goldberg, Phys. Rev. **109**, 331 (1958).
[29] R. A. Laff and H. Y. Fan, Phys. Rev. **112**, 317 (1958).
[30] F. S. Ham, Phys. Rev. **100**, 1251(A) (1955).
[31] See, for example, D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).

TABLE V. Values of the mass and scattering-time anisotropy factors K and L and the statistical-scattering factor G calculated from the experimental data assuming the ⟨110⟩ general-ellipsoid multivalley model with the condition $b'+c'=0$.

Parameter	Room temperature	77°K
K_1	1.71	1.65
L_1	0.29	0.35
G_1	0.96	0.90
K_2	3.39	2.98
L_2	0.58	0.60
G_2	1.12	0.98

or

$$M_{100}=G\frac{6K_2^2(K_2-1)^2}{(2K_2^2+2K_2-1)^2}, \tag{19}$$

$$M_{110}=M_{100}/2, \tag{20}$$

$$M_{100}{}^{001}(=M_{110}{}^{001})=G\frac{3K_2^2}{(2K_2^2+2K_2-1)}-1, \tag{21}$$

and

$$M_{110}{}^{1\bar{1}0}=M_{110}+M_{110}{}^{001}. \tag{22}$$

The least-squares analyses of these systems of equations and the experimental data yielded the values listed in Table V. One solution leads to a G value less than unity at 77°K, the other to G values less than unity at both temperatures. This is further evidence that the ⟨110⟩ general-ellipsoid model does not apply to the valence band of PbTe.

(5) Effective-Mass Components at 77°K

The degenerate statistics occurring at 77°K make it possible to attempt a calculation of the individual effective-mass components in p-type PbTe, not merely their ratios. We used a generalization of a formula first derived by Sommerfeld[32] when he applied Fermi-Dirac statistics to the transport equation and calculated an approximation for highly-degenerate statistics. The generalization consists of expressing the result for the law $\tau\propto E^r$ and including the effects of mass and τ anisotropy. The result again has the form of Eq. (3) or (4), except that

$$G=1+\frac{\pi^2r^2}{3}\left(\frac{kT}{E_F}\right)^2, \tag{23}$$

where k is Boltzmann's constant, T is the absolute temperature, and E_F is the Fermi-level energy. The Fermi level for a multivalley ellipsoid-of-revolution model is given by

$$E_F=\frac{h^2}{2m_0(m_t{}^{*2}m_l{}^{*})^{\frac{1}{3}}}\left(\frac{3n_v}{8\pi}\right)^{\frac{2}{3}}, \tag{24}$$

where h is Planck's constant, $m_t{}^{*}$ and $m_l{}^{*}$ are the transverse and longitudinal effective-mass components (relative to the free-electron mass m_0) in the principal-axis system of a valley, and n_v is the carrier concentration per valley. We used the carrier concentration obtained from the Hall data at 77°K, neglected anisotropy in the scattering time, and assumed $r=-0.5$, which is appropriate for acoustical mode lattice scattering. From Eqs. (23) and (24) and the experimental G value at 77°K we obtained $m_t{}^{*}=0.11$ and $m_t{}^{*}=0.025$ for eight ellipsoids, and $m_t{}^{*}=0.17$ and $m_t{}^{*}=0.040$ for four ellipsoids. The total density-of-states effective mass in either case is $0.16\,m_0$.

If we assume that the carrier concentration, effective mass, and scattering law do not change with temperature, we may calculate a room temperature G value, using tables of Fermi-Dirac integrals. (Neither the approximation of highly degenerate nor strictly-classical statistics is applicable at room temperature.) We obtained $G=1.14$, which is in reasonable agreement with the value of 1.17 derived directly from the experimental data.

We cannot claim much accuracy for this effective-mass calculation, particularly in view of the arbitrary assumption of $r=-0.5$, a choice dictated by the limited number of exponents for which the Fermi-Dirac integrals have been tabulated. However, the results are not unreasonable, since we find that all except one (Shogenji and Uchiyama[33]) of the estimates of density-of-state effective masses in the conduction and valence bands of the lead salts lie in the range $0.10m_0$ $-0.36m_0$.[33–40] Estimates of the geometric mean of the electron and hole effective-masses in PbTe[37,38] range from $0.16m_0$ to $0.27m_0$. Our value for the holes coupled with an estimate of $0.325m_0$ for electrons[39] leads to a geometric mean of $0.23m_0$.

PRELIMINARY RESULTS FOR n-TYPE PbTe AND FOR PbS AND PbSe

We would like to mention briefly some preliminary room-temperature data we have obtained on n-type PbTe and on n- and p-type PbS and PbSe. The samples used were all grown by the Bridgman-Stockbarger technique. We include these results now because they were unexpected, and because it may be some time before we can obtain crystals of as good a quality as the p-type PbTe material.

Some approximate, representative values are listed in Table VI. (The results for p-type PbTe are also

[32] A. Sommerfeld, Z. Physik **47**, 1, 43 (1927).

[33] K. Shogenji and S. Uchiyama, J. Phys. Soc. (Japan) **12**, 252 (1957).

[34] E. H. Putley, Proc. Phys. Soc. (London) **B68**, 35 (1955).

[35] J. Bloem, F. A. Kröger, and H. J. Vink, *Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 273.

[36] R. L. Petritz and W. W. Scanlon, Phys. Rev. **97**, 1620 (1955).

[37] R. A. Smith, Physica **20**, 910 (1954).

[38] G. G. Macfarlane and L. Pincherle (unpublished), quoted by T. S. Moss, Proc. Inst. Radio Engrs. **43**, 1869 (1955).

[39] E. Z. Gershtein, T. S. Stavitskaia, and L. S. Stil'bans, Zhur. Tekh. Fiz. **26**, 2472 (1957) [translation: Soviet Phys.—Tech. Phys. **2**, 2302 (1957)].

[40] D. M. Finlayson and D. Greig, Proc. Phys. Soc. (London) **73**, 49 (1959).

TABLE VI. Approximate values of room-temperature weak-field magnetoresistance in the lead salts.

Material	Coefficient M_{110}	M_{110}^{001}	$M_{110}^{1\bar{1}0}$	M_{100}	M_{100}^{001}
n-PbS	0.01	0.08	0.09		
p-PbS	0.02	0.10	0.11		
n-PbSe	0.02	0.09	0.10		
p-PbSe	0.03	0.09	0.12	0.05	0.09
n-PbTe				0.35	0.18
p-PbTe	0.28	0.35	0.61	0.53	0.35

given for comparison.) The surprising result is the relatively small room-temperature longitudinal magnetoresistance in PbS and PbSe, both n- and p-type, perhaps ten times smaller than in p-type PbTe at this temperature. Our earlier work at 77° and 4.2°K[1] suggested that the longitudinal coefficients were as large or larger than the transverse in all three lead salts, and that the magnitude of each coefficient did not vary greatly from one material to the next.

The newer, room-temperature data are not necessarily grossly inconsistent with the older results at 77°K. For the smaller anisotropy suggested by the newer results, Eqs. (6) through (9) predict a relatively large increase in the ratio of a longitudinal to a transverse coefficient as the temperature is lowered and the statistics become degenerate. However, all of the earlier data at 77°K are probably too large; for example, the earlier results for p-type PbTe were $M_{100}\approx 0.44$ and $M_{100}^{001}\approx 0.21$, whereas the results reported in this paper are 0.41 and 0.15, respectively.

Despite the improved experimental techniques used for the room temperature results, the longitudinal coefficients were so small that they may well be in error by a factor of two, and hence the data cannot be used to select a band model. It is clear nevertheless that the magnitude of the room-temperature magnetoresistance in PbS and PbSe is much different from that in PbTe, and we hope that eventually it will be possible to relate this difference to the anomalous band-gap sequence in the lead salts.

CONCLUSIONS

We have made a thorough study of the magnetoresistance in p-type PbTe, using six crystals from an ingot which was pulled from the melt. We believe that the sample quality was considerably better than that of the crystals used for our earlier work, and that this had an important bearing on the accuracy of the data obtained.

We found that the general predictions of weak-field theory in cubically-symmetric crystals were closely obeyed at room temperature and 77°K over the range of magnetic-field values to which the theory applies, and we observed deviations at higher fields at 77°K which were of the types predicted by Gold and Roth.[21] Their theory can present closed expressions for the magnetoresistance at arbitrary magnetic-field strengths because it makes the simplifying assumption that the scattering time is constant. We had the rather unusual opportunity of working under conditions of highly degenerate statistics which make the constant scattering-time a realistic approximation.

The close conformity at two temperatures to the symmetry relation for the ⟨111⟩ ellipsoid-of-revolution multivalley model suggests as strongly as is possible from magnetoresistance data alone that this model is appropriate for the valence band of PbTe. Assuming this model, we were then able to calculate reasonable values of the anisotropy ratio K and the statistical-scattering factor G. We also made a crude attempt to determine the absolute values of the effective-mass components, and we believe that this type of calculation, under the proper conditions, could become a useful method for obtaining a quick estimate of effective masses in low-resistivity crystals.

We look forward to successful cyclotron-resonance, piezoresistance, magnetoacoustic, or other measurements which will confirm or contradict our conclusions on the valence-band structure of PbTe.

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